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MEMORANDUM FOR PRR (Contractor Publication)

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SUBJECT: Authorization for Release of Technical Information, Control Number: AFRL-PR-ED-TP-FY99-0045A
K.O. Christe, D.A. Dixon et al. (RSTX) and J.A. Sheehy, "A Quantitative Scale for the Strength of Lewis Acids"
and "On the Reaction of N_2F^+ with HN_3 and the Synthesis and Characterization of $N_5^+AsF_6^-$ "
Presentation (Statement A)

A QUANTITATIVE SCALE FOR THE STRENGTH OF LEWIS ACIDS

KARL O. CHRISTE, DAVID A. DIXON, DOUGLAS McLEMORE

ON THE REACTION OF N_2F^+ WITH HN_3 AND
THE SYNTHESIS AND CHARACTERIZATION OF $N_5^+AsF_6^-$

KARL O. CHRISTE, WILLIAM W. WILSON, JEFFREY A. SHEEHY

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QUANTITATIVE SCALE FOR THE STRENGTH OF LEWIS ACIDS

TWO TYPES OF ACIDS

- BRONSTED OR PROTIC ACIDS (PROTON DONORS)



QUANTITATIVE SCALES ARE KNOWN : pH AND pK SCALES

IONIC PRODUCT OF H₂O

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 10^{-14}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

$$\text{p}K_\alpha = -\log K_\alpha = [\text{H}^+][\text{A}^-]/[\text{HA}]$$

- LEWIS ACIDS (ELECTRON ACCEPTORS)



STRENGTH IS DIFFICULT TO MEASURE

NO QUANTITATIVE SCALE KNOWN

PROPOSED LEWIS ACID STRENGTH SCALE

- F⁻ ION IS A VERY STRONG LEWIS BASE
 - HAS A SMALL DIAMETER
 - INTERACTS WITH MOST LEWIS ACIDS
 - IS WELL SUITED FOR THEORETICAL CALCULATIONS
- F⁻ AFFINITY (FA) INCREASES WITH LEWIS ACID STRENGTH AND, THEREFORE, CAN SERVE AS A BASIS FOR A QUANTITATIVE LEWIS ACIDITY SCALE
- ONLY FEW F⁻ AFFINITY DATA WERE AVAILABLE ESPECIALLY FOR INORGANICS;
 - MANY WERE ONLY QUALITATIVE (CYCLOTRON RESONANCE BRACKETING AND EQUILIBRIUM MEASUREMENTS)
 - LARGE ERRORS AND DIFFERENT METHODS GAVE DIFFERENT RESULTS
- NEEDED
 - A QUANTITATIVE, INTERNALLY CONSISTENT SET OF FA'S FOR ANY DESIRED LEWIS ACID

METHODS FOR CONSTRUCTION OF QUANTITATIVE F⁻ AFFINITY SCALE

- THEORETICAL CALCULATIONS, USING POLARIZED DOUBLE-ZETA BASIS SETS, WERE PERFORMED AT THE FOLLOWING LEVELS

LDF

NLDF

MP2

- TO SIMPLIFY THE CALCULATIONS, BECAUSE THE ELECTRON AFFINITY OF F IS HARD TO CALCULATE, COF₂ WAS USED AS A REFERENCE COMPOUND



- TO CONVERT TO ABSOLUTE VALUES, THE EXPERIMENTALLY KNOWN FA OF COF₂ (49.9 kcal/mol) WAS ADDED TO THE RELATIVE FA VALUES

PROPOSAL OF A pF SCALE FOR LEWIS ACIDITY

- F⁻ AFFINITIES WERE CALCULATED FOR 106 LEWIS ACIDS AND RANGE FROM 0 - 120 kcal/mol ON THE ABSOLUTE SCALE GIVING A VALUE OF FA (AlF₃) = 115 kcal/mol, THE SAME AS DETERMINED BY THERMODYNAMIC

EXPERIMENT

- TO OBTAIN A LEWIS ACIDITY SCALE RANGE COMPARABLE TO THE FAMILIAR pH SCALE RANGE OF 0-14, THE FOLLOWING CONVENTION IS

PROPOSED

$$pF = \frac{F^- \text{ AFFINITY (kcal/mol)}}{10}$$

GIVING A pF RANGE OF 0-12, WITH 12 BEING THE VALUE FOR THE STRONGEST KNOWN LEWIS ACID (SbF₅)

ABBREVIATED pF SCALE

(CHRISTE, DIXON, McLEMORE)

COMPOUND	pF	COMPOUND	pF	COMPOUND	pF
SbF ₅	12.03	cis-IO ₂ F ₃	9.66	SOF ₄	6.60
AlF ₃	11.50	PF ₅	9.49	XeOF ₄	6.37
AlFCl ₂	11.50	SeOF ₄	8.69	TeF ₆	6.15
AlF ₂ Cl	11.47	TeF ₄	8.34	POF ₃	5.86
AlCl ₃	11.46	BF ₃	8.31	XeF ₄	5.71
TeOF ₄	10.79	GeF ₄	8.30	SF ₄	5.67
InF ₃	10.75	ClF ₅	7.47	COF ₂	4.99
GaF ₃	10.70	BrF ₃	7.35	PF ₃	4.49
AsF ₅	10.59	SiF ₄	7.35	HF	3.68
SnF ₄	9.82	SeF ₄	7.12	NO ₂ F	1.92
				NOF	1.74

SPECIAL COMMENTS ABOUT THE pF SCALE

- pF VALUES ARE FOR THE FREE ISOLATED MOLECULES
- VALUES FOR ASSOCIATED SOLIDS MUST BE CORRECTED
- FORMATION OF COMPLEX FLUORO ANIONS CAN BE CORRELATED WITH
THE pF SCALE AND BECOMES DIFFICULT BELOW pF ~ 3.5
- PREPRINTS OF PAPER SHOULD BECOME AVAILABLE WITHIN 4-8 WEEKS

N_2F^+ CHEMISTRY AND SYNTHESIS OF $\text{N}_5^+\text{AsF}_6^-$

- HOMOLEPTIC POLYNITROGEN COMPOUNDS ARE OF GREAT INTEREST FOR HIGH ENERGY DENSITY MATERIALS (HEDM)
- MANY THEORETICAL STUDIES DURING THE PAST 15 YEARS HAVE BEEN DONE, BUT NO SUCCESSFUL SYNTHESIS OF A HOMOLEPTIC POLYNITROGEN HEDM HAS BEEN REPORTED
- ONLY TWO HOMOLEPTIC POLYNITROGEN COMPOUNDS ARE KNOWN WHICH CAN BE PREPARED IN SUBSTANCE

N_2	1772	RUTHERFORD, SCHEELE, CAVENDISH
N_3^-	1890	CURTIUS

PROBLEMS WITH SYNTHESIS OF POLYNITROGEN HEDM

- ALL THE ENERGY MUST COME FROM ENDOTHERMICITY WHICH MAKES POLYNITROGEN HEDM EXTREMELY DANGEROUS
- (SENSITIVITY INCREASES WITH INCREASING ENERGY)
- BASIS FOR HIGH ENERGY CONTENT ARE THE LARGE DIFFERENCES IN BOND

ENERGIES FOR N-N BONDS

N-N	38 kcal/mol	C-C	85 kcal/mol
N=N	100 kcal/mol	C=C	143 kcal/mol
N≡N	228 kcal/mol	C≡C	194 kcal/mol
$\begin{array}{c} \text{-(N=N)}_n \text{-} \\ 38 + 100 \end{array}$	$\begin{array}{c} \xrightarrow{-90} \\ \text{N}\equiv\text{N} \\ 228 \end{array}$	$\begin{array}{c} \text{-(CH=CH)}_n \text{-} \\ 85 + 143 \end{array}$	$\begin{array}{c} \xrightarrow{+34} \\ \text{CH}\equiv\text{CH} \\ 194 \end{array}$

EXCEPTIONS: N₂, O₂

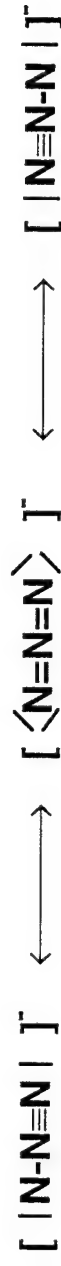
STABLE MONOMERS
UNSTABLE POLYMERS

NORMAL CASE:

STABLE POLYMERS
UNSTABLE MONOMERS

GENERAL CONCEPT FOR POLYNITROGEN HEDM SYNTHESIS

- ALL POLYNITROGEN COMPOUNDS ARE UNSTABLE WITH RESPECT TO N_2
- ACTIVATION ENERGY BARRIER TOWARD N_2 ELIMINATION IS DETERMINED BY THE WEAKEST BOND IN POLYNITROGEN COMPOUND
- THE BARRIER AND METASTABILITY OF POLYNITROGEN COMPOUNDS MUST BE INCREASED BY SUITABLE RESONANCE STRUCTURES



- DOUBLE BOND CHARACTER OF N-N BONDS IN AZIDE ION EXPLAINS ITS EXCEPTIONAL STABILITY
- HOW CAN THIS STABILIZATION EFFECT BE TAKEN ADVANTAGE OF?

EXPANSION OF THE AZIDE STRUCTURE

- ADDITION OF $[N_2]^+$ UNITS TO N_3^-



- HOWEVER, THEORETICAL CALCULATIONS SHOW THAT $D_{\infty h} N_4$ IS NOT STABLE

$[\text{N}=\text{N}=\text{N}]^-$ NEIGHBORING CHARGES OF EQUAL SIGN MUST BE AVOIDED
 $(-)(+)(+)(-)$

- NO PLAUSIBLE RESONANCE STRUCTURES CAN BE WRITTEN FOR N_4 WHICH
 RETAIN DOUBLE BOND CHARACTER WHILE AVOIDING NEIGHBORING CHARGES
 OF EQUAL SIGN

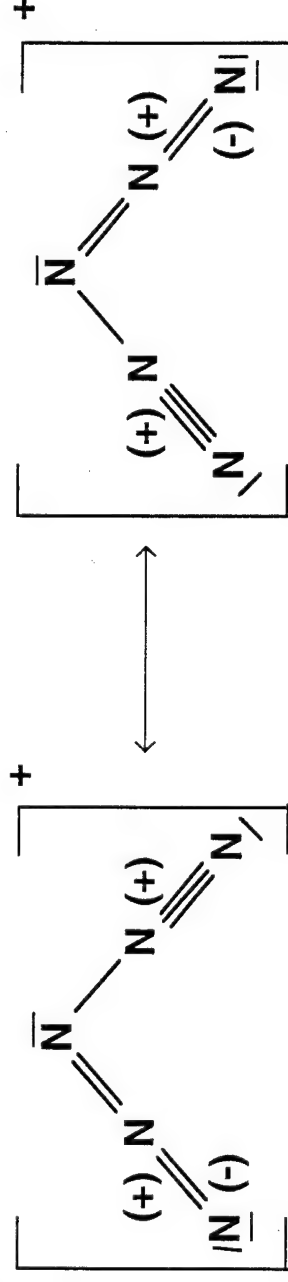
EXPANSION OF THE AZIDE STRUCTURE TO N_5^+

- THE SAME PROBLEM EXISTS FOR N_5^+ WITH NEIGHBORING POSITIVE CHARGES



- RESONANCE STRUCTURES, HOWEVER, CAN BE WRITTEN WHICH AVOID THIS

PROBLEM



- AB INITIO CALCULATIONS (CCSD(T) AND B3LYP) CONFIRM THE STABILITY OF THIS

C_{2v} STRUCTURE

SELECTION OF SUITABLE STARTING MATERIALS FOR N_5^+ SYNTHESIS

- REQUIREMENTS

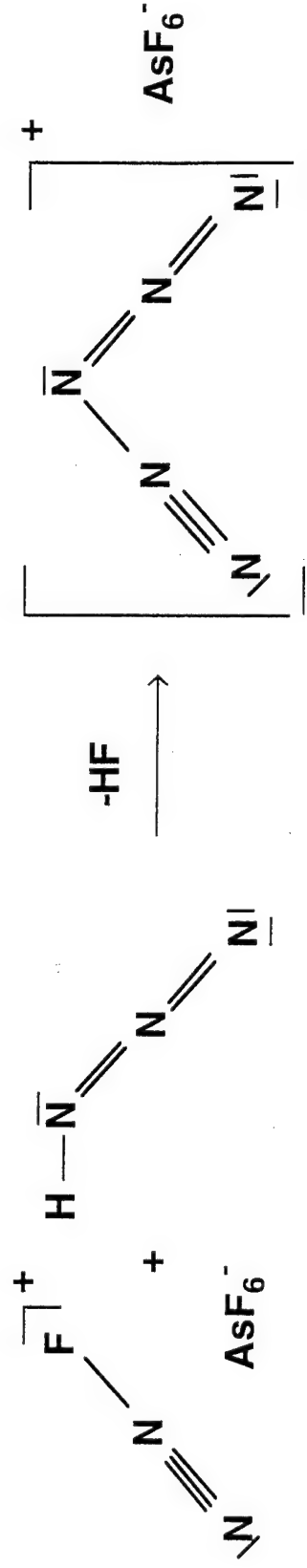
STARTING FRAGMENTS MUST HAVE ALREADY BUILT IN WEAKENED BONDS

MUST HAVE A FORMAL POSITIVE CHARGE (IP OF $N_2 = 359$ kcal/mol)

COUPLING REACTION MUST BE EXOTHERMIC

CHOICE OF SUITABLE SOLVENT (HEAT SINK, STABILIZATION, SAFETY)

- IDEAL CANDIDATE SYSTEM



ACTUAL SYNTHESIS OF $\text{N}_5^+ \text{AsF}_6^-$

- SYSTEM WORKED AS PLANNED



HIGH YIELD

ONLY OTHER BYPRODUCT 20-40% $\text{H}_2\text{N}_3^+ \text{AsF}_6^-$

2 MMOL (0.5 G SCALE)

- PROPERTIES OF $\text{N}_5^+ \text{AsF}_6^-$

WHITE SOLID

SPARINGLY SOLUBLE IN HF

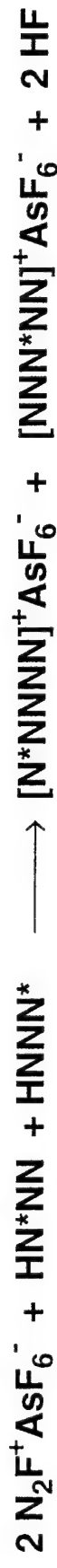
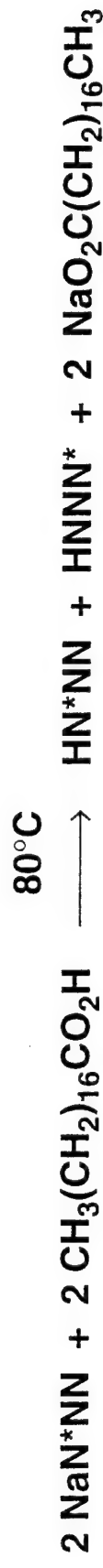
MARGINALLY STABLE AT 22 °C

HIGHLY ENERGETIC

REACTS VIOLENTLY WITH WATER AND ORGANICS

CALCULATED $\Delta H_f^\circ \text{N}_5^+ = 353 \text{ kcal/mol}$

SYNTHESIS OF ^{15}N LABELED $\text{N}_5^+\text{AsF}_6^-$



^{15}N LABELED N_5AsF_6 NEEDED FOR POSITIVE IDENTIFICATION OF

N_5^+ BY SPECTROSCOPIC METHODS

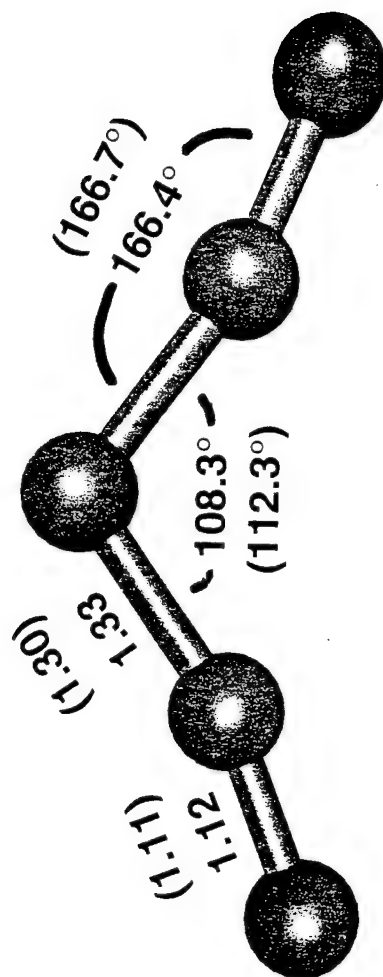
CHARACTERIZATION OF $\text{N}_5^+ \text{AsF}_6^-$

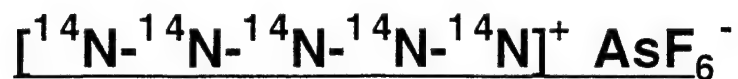
- ^{14}N AND ^{15}N NMR SPECTRA
- LOW-TEMPERATURE RAMAN AND INFRARED SPECTRA OF NORMAL AND ISOTOPICALLY LABELED N_5^+
- NORMAL COORDINATE ANALYSIS
- MASS SPECTROSCOPY
- THEORETICAL CALCULATIONS
 - OPTIMIZED GEOMETRY
 - VIBRATIONAL SPECTRA
 - ISOTOPIC SHIFTS
 - NMR SHIFTS
 - HEAT OF FORMATION



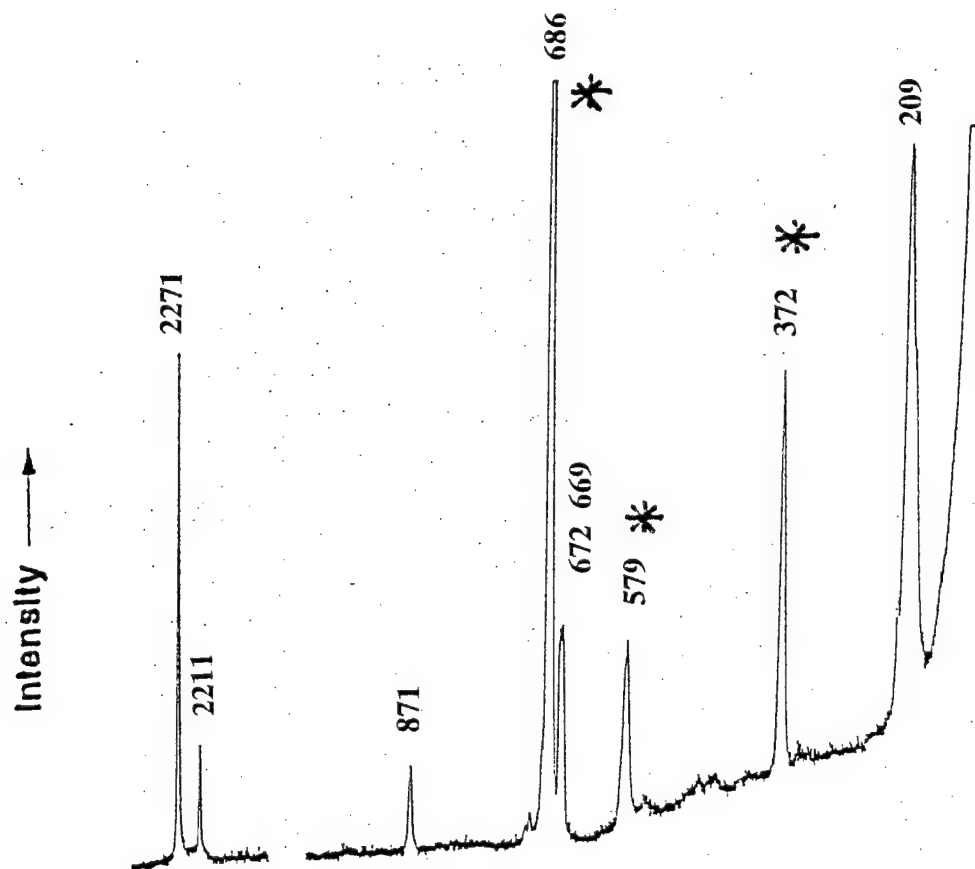
PHOTOGRAPH OF N_5AsF_6 IN QUARTZ TUBE

OPTIMIZED GEOMETRIES FOR N_5^+ CCSD(T) (B3LYP) VALUES





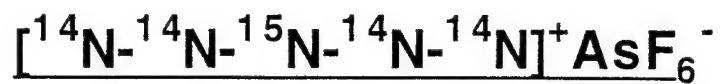
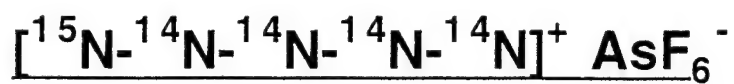
LOW-TEMPERATURE RAMAN SPECTRUM



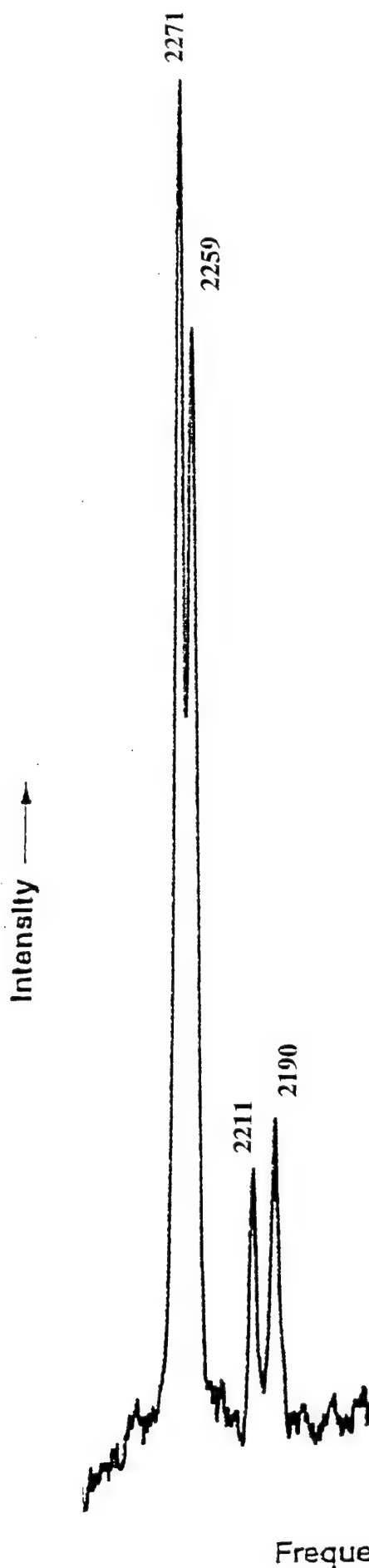
* = AsF_6^-

Frequency, cm^{-1}

N_5^+	OBSD (cm^{-1})	CCSD(T) (cm^{-1})	B3LYP (cm^{-1})
$\nu_1 (\text{A1})$	2271	2229	2336
$\nu_7 (\text{B2})$	2211	2175	2282
$\nu_2 (\text{A1})$	871	818	850
$\nu_4 (\text{A1})$	209	181	193



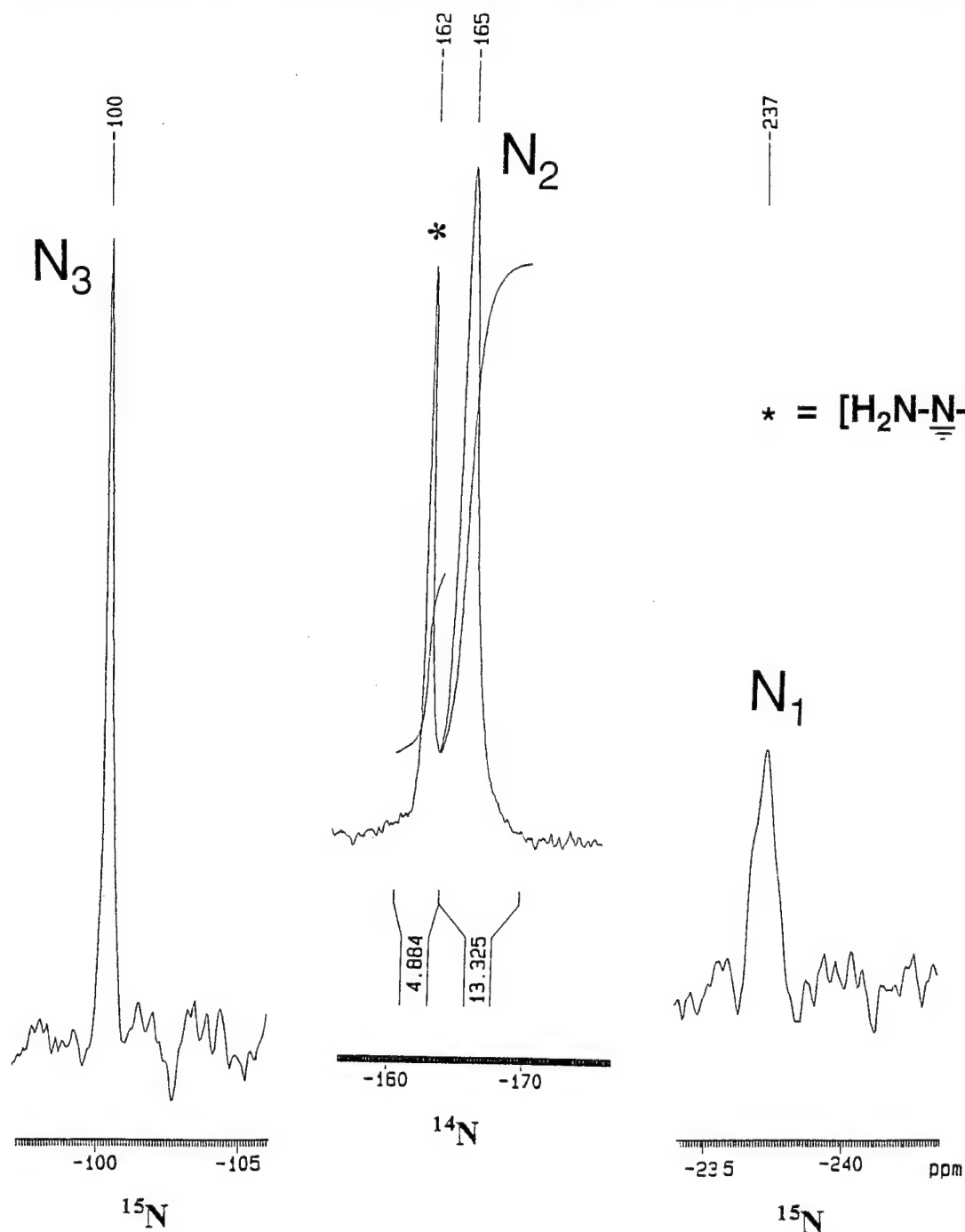
LOW-TEMPERATURE RAMAN SPECTRUM



14N-15N SHIFTS (cm^{-1})

	OBSD	CALCD
ν_1	12	11.8
ν_7	21	21.4
ν_2	14	14.1

NITROGEN NMR SPECTRA OF

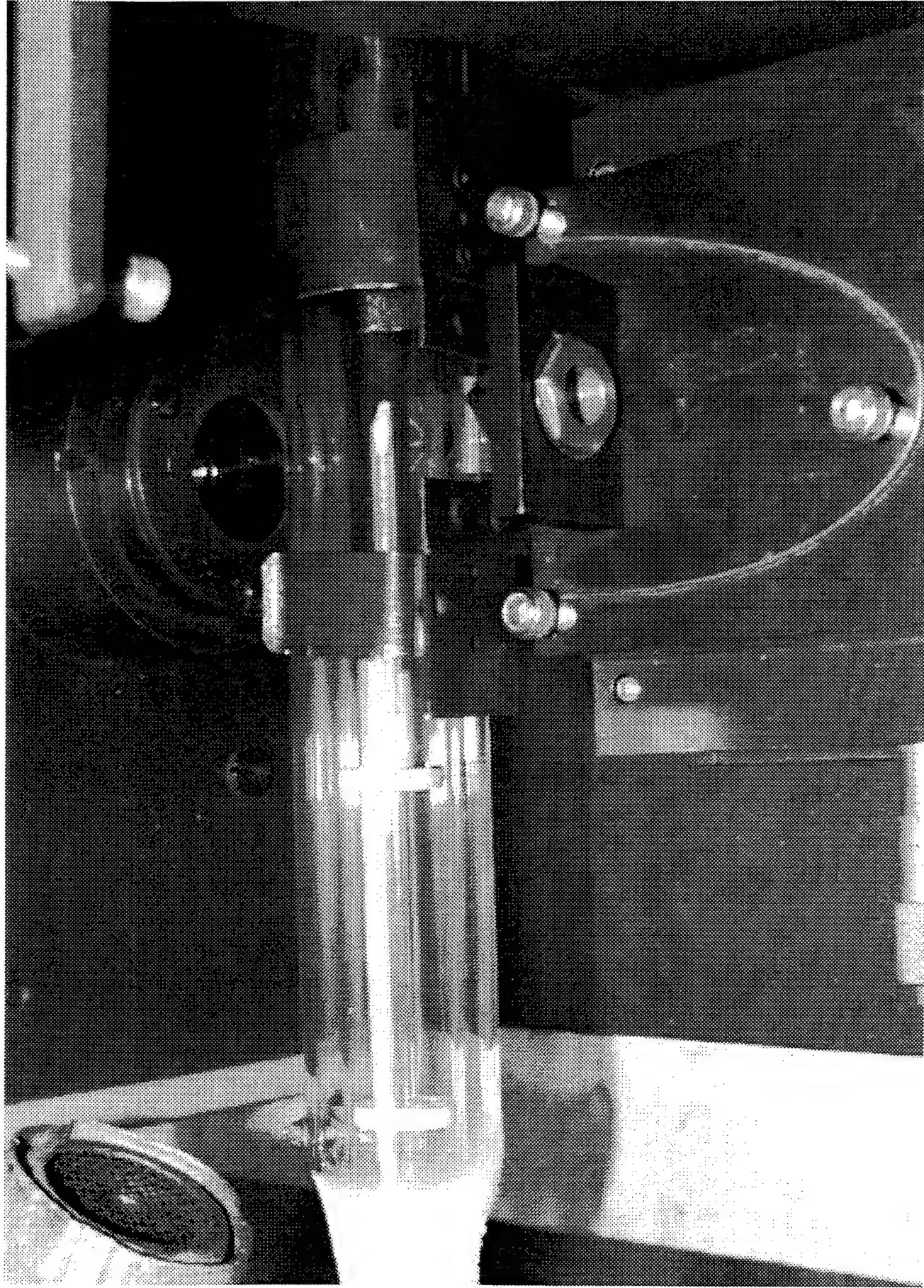


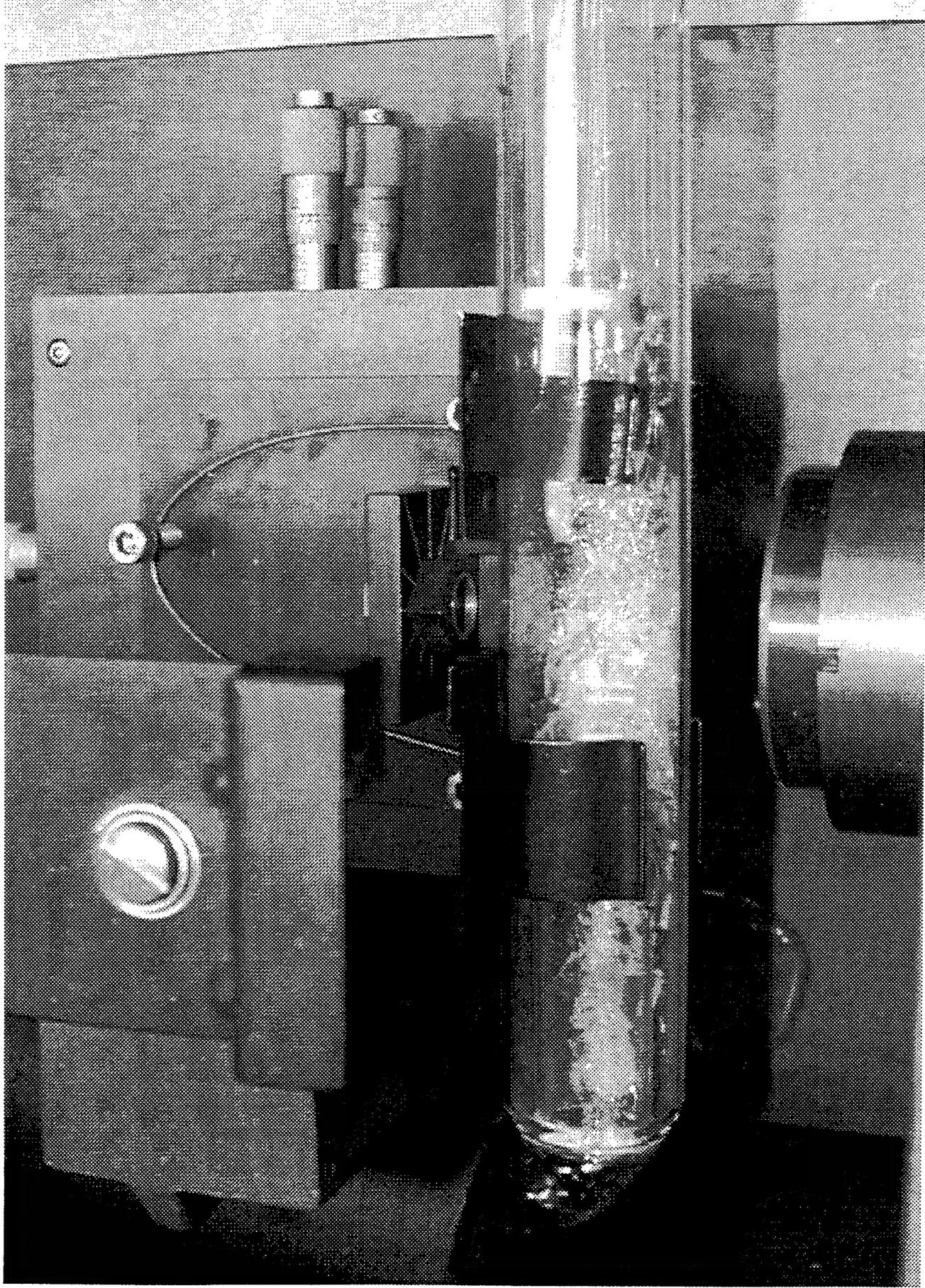
NMR SHIFTS (ppm)

OBSD

CALCD

N_1	-237.3	-235
N_2	-165.3	-166
N_3	-100.4	-95





WORK IN PROGRESS

- SYNTHESIS OF $\text{N}_5^+ \text{SbF}_6^-$
- SENSITIVITY AND SAFETY DATA
- COMBINATION OF N_5^+ WITH POLYNITROGEN ANIONS
TO PREPARE FIRST ALLOTROPE OF N_2
- SYNTHESIS OF XeN_3^+

SUMMARY

- A QUANTITATIVE SCALE FOR THE STRENGTH OF LEWIS ACIDS WAS DEVELOPED
- $\text{N}_5^+\text{AsF}_6^-$, THE ONLY HOMOLEPTIC POLYNITROGEN COMPOUND BESIDES N_2 AND N_3^- WHICH CAN BE MADE IN BULK, WAS PREPARED FROM $\text{N}_2\text{F}^+\text{AsF}_6^-$ AND HN_3 AND WAS CHARACTERIZED
- N_5^+ HAS A V-SHAPED CHAIN STRUCTURE AND IS marginally stable at room temperature

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